

# Subband filling and Mott transition in $\text{Ca}_{2-x}\text{Sr}_x\text{RuO}_4$

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A new concept is proposed for the paramagnetic metal insulator transition in the layer perovskite  $\text{Ca}_{2-x}\text{Sr}_x\text{RuO}_4$ . Whereas the pure Sr compound is metallic up to very large Coulomb energies due to strong orbital fluctuations, structural changes induced by doping with Ca give rise to a interorbital charge transfer which makes the material extremely sensitive to local correlations. Using dynamical mean field theory based on finite temperature multi-band exact diagonalization it is shown that the combination of crystal field splitting and onsite Coulomb interactions leads to complete filling of the  $d_{xy}$  band and to a Mott transition in the half-filled  $d_{xz,yz}$  bands.

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The layer perovskite  $\text{Ca}_{2-x}\text{Sr}_x\text{RuO}_4$  has attracted wide interest during recent years because of the complex sequence of electronic and magnetic phases which arise when Sr is iso-electronically substituted by Ca [1, 2, 3]. While the pure Sr compound exhibits unconventional superconductivity [4], the structural distortions induced by the smaller Ca ions ultimately lead to an antiferromagnetic Mott insulator. The physical mechanism of how this multi-band material with four electrons per Ru ion evolves from the metal  $\text{Sr}_2\text{RuO}_4$  towards the insulator  $\text{Ca}_2\text{RuO}_4$  is presently not well understood.

According to band structure calculations [5] the  $t_{2g}$  orbitals in  $\text{Sr}_2\text{RuO}_4$  are approximately equally occupied. Because of the planar geometry, these bands split into a wide, nearly two-dimensional  $d_{xy}$  band and two narrow, nearly one-dimensional  $d_{xz,yz}$  bands. Clearly, the Mott transition in such a highly anisotropic system cannot be understood in terms of single-band models, or multi-band extensions assuming degenerate subbands. To analyze the role of local Coulomb interactions in  $\text{Ca}_{2-x}\text{Sr}_x\text{RuO}_4$  several aspects were investigated within dynamical mean field theory (DMFT) [6], using a variety of impurity solvers to treat onsite correlations [7, 8, 9, 10, 11, 12].

While it is generally agreed upon that Coulomb interactions in  $\text{Sr}_2\text{RuO}_4$  lead to a sizeable band narrowing and effective mass enhancement, and a shift of the  $d_{xy}$  van Hove singularity towards the Fermi level due to  $d_{xz,yz} \rightarrow d_{xy}$  charge transfer [7, 9, 10, 11], the Mott transition near the Ca end of the phase diagram is complicated because of the charge rearrangement among  $t_{2g}$  orbitals when the Ca/Sr concentration is varied. Using the non-crossing approximation [13], Anisimov *et al.* [8] obtained successive, ‘orbital selective’ Mott transitions upon increasing the onsite Coulomb energy  $U$ : first for the narrow  $d_{xz,yz}$  bands and subsequently for the wide  $d_{xy}$  band. These transitions arise via a  $d_{xy} \rightarrow d_{xz,yz}$  charge transfer, i.e.,  $(n_{xy}, n_{xz}, n_{yz}) \approx (2/3, 2/3, 2/3) \rightarrow (0.5, 0.75, 0.75)$ . Orbital selective Mott transitions, with the same interorbital charge transfer, were found also by Dai *et al.* [12] within slave boson mean field calculations for a three-

band model consisting of wide and narrow semi-circular densities of states. To account for the Ca induced octahedral distortions [14], the  $d_{xy}$  band was assumed to be narrower than the  $d_{xz,yz}$  bands. Accordingly, in contrast to Ref. [8],  $d_{xy}$  is the first band to become insulating with increasing  $U$ . An important parameter in this work is the crystal field splitting  $\Delta$  between  $t_{2g}$  orbitals, which yields Mott transitions at much smaller values of  $U$  than for  $\Delta = 0$ . In both models, a second interorbital charge transfer due to additional structural modifications, i.e.,  $(n_{xy}, n_{xz}, n_{yz}) = (0.5, 0.75, 0.75) \rightarrow (1.0, 0.5, 0.5)$ , is required in the limit  $x \rightarrow 0$  to yield the antiferromagnetic insulating properties of  $\text{Ca}_2\text{RuO}_4$  [8].

In the present work, we use finite temperature exact diagonalization (ED) DMFT [15] to study the nature of the Mott transition in  $\text{Ca}_{2-x}\text{Sr}_x\text{RuO}_4$ . Since a  $t_{2g}$  tight-binding Hamiltonian including the full complexity of the octahedral distortions as a function of Ca/Sr concentration is not yet available, we use the  $\text{Sr}_2\text{RuO}_4$  density of states components as a single-particle starting point (see Fig. 1). As shown by Fang *et al.* [14], a key effect caused by rotation, tilting and flattening of oxygen octahedra is the *increasing*  $d_{xy}$  orbital occupancy with increasing Ca concentration: In the limit  $x = 0$  (pure Ca), the spin-averaged occupancy is about  $n_{xy} \approx 0.83$ , compared to  $n_{xy} \approx 0.64$  for  $x = 2$  (pure Sr). To account for this charge transfer, we allow, as in Ref. [12], for a crystal field splitting  $\Delta$  between  $d_{xy}$  and  $d_{xz,yz}$  states. For instance, a lowering of the  $d_{xy}$  bands by  $\Delta = 0.2$  (0.4) eV yields  $n_{xy} \approx 0.74$  (0.83). The total occupancy of the  $t_{2g}$  bands is four, independently of Ca/Sr concentration.

The main result of this work is a new mechanism for the Mott transition in this multi-band system: For realistic values of the Coulomb energy  $U$  and crystal field splitting  $\Delta$ , we find a gradual filling of the  $d_{xy}$  subband with increasing  $U$ . Once the  $d_{xz,yz} \rightarrow d_{xy}$  charge transfer is complete, i.e.,  $(n_{xy}, n_{xz}, n_{yz}) \rightarrow (1.0, 0.5, 0.5)$ , a Mott transition takes place in the remaining half-filled  $d_{xz,yz}$  bands. The critical Coulomb energy at which this transition occurs is lower for larger crystal field  $\Delta$ .

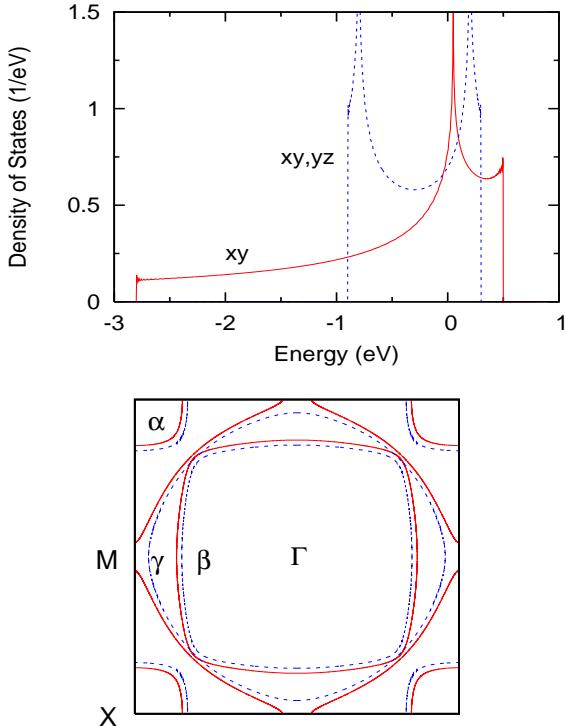


FIG. 1: Upper panel: Density of states of Sr<sub>2</sub>RuO<sub>4</sub>. Solid (red) curve: wide  $d_{xy}$  band; dashed (blue) curve: narrow  $d_{xz,yz}$  bands ( $E_F = 0$ ). Lower panel: Fermi surface (schematic) of Sr<sub>2</sub>RuO<sub>4</sub> (dashed blue curve) and Ca<sub>1.5</sub>Sr<sub>0.5</sub>RuO<sub>4</sub> (solid red curve). In the former (latter) case, the  $d_{xy}$  van Hove singularity at M is above (below)  $E_F$ .

This scenario is qualitatively different from the ones proposed in Refs. [8, 12]: Instead of successive transitions in the half-filled  $d_{xy}$  band and in the 3/4-filled  $d_{xz,yz}$  bands, we find a common  $d_{xy}$  band filling and  $d_{xz,yz}$  Mott transition. The  $d_{xy}$  band filling, induced by the combined effect of crystal field and Coulomb interactions, signifies a change from a correlated metallic state to a correlated band insulating state and does not correspond to a Mott transition. On the other hand, since a full  $d_{xy}$  band implies half-filled  $d_{xz,yz}$  bands, the latter readily undergo a standard metal insulator transition. Thus, the present three-band system does not exhibit orbital selective Mott transitions. Our solution solely relies on the structure induced increase in  $d_{xy}$  occupancy [14] and is consistent with the  $(n_{xy}, n_{xz}, n_{yz}) = (1.0, 0.5, 0.5)$  configuration obtained for Ca<sub>2</sub>RuO<sub>4</sub> within LDA+U [8]. Thus, we do not require the more complex path  $n_{xy} \approx 2/3 \rightarrow 1/2 \rightarrow 1$  as Sr is replaced by Ca.

The details of our multi-band ED approach are given in Ref. [15]. Exploiting the sparseness of the impurity Hamiltonian, much larger clusters representing the bath can now be handled, thereby significantly reducing finite size effects. All calculations are carried out for full Hund exchange  $J$ . To obtain the orbital occupancy  $n_i$  as a

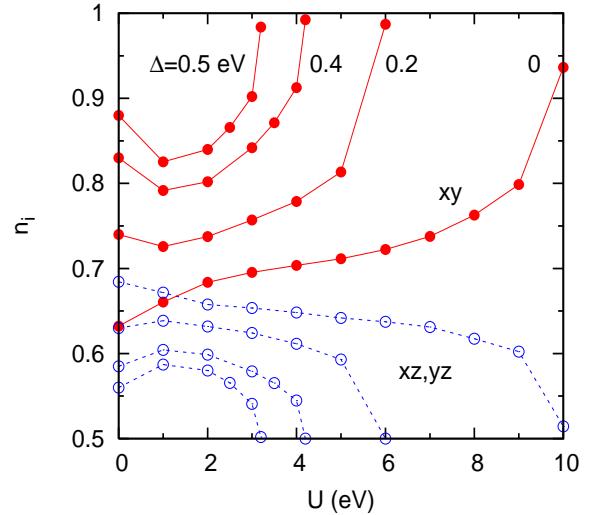


FIG. 2: Orbital occupancy  $n_i$  as a function of Coulomb energy for various crystal field splittings  $\Delta$ , derived within ED/DMFT for  $T = 20$  meV. Solid (red) dots:  $n_{xy}$ , empty (blue) dots:  $n_{xz,yz}$ . The lines are guides to the eye.

function of  $U$ , for a particular  $\Delta$ , we assume  $J = U/4$ . The interorbital Coulomb energy is  $U' = U - 2J$ . To achieve fast convergence we use the cluster size  $n_s = 9$  (2 bath levels per impurity orbital); for greater precision specific points are calculated with  $n_s = 12$ . The temperature is assumed to be  $T = 20$  meV. We focus here on the paramagnetic Mott transition.

Fig. 1 shows the  $t_{2g}$  density of states components for Sr<sub>2</sub>RuO<sub>4</sub>, derived from a tight-binding Hamiltonian [7] fitted to the LDA band structure of Ref. [5]. The band extrema were adjusted slightly in order to accommodate four electrons below  $E_F$ . The  $d_{xy}$  van Hove singularity lies about 60 meV above  $E_F$ . The lower panel shows the Fermi surface. The  $\gamma$  sheet corresponds to  $d_{xy}$ , the  $\alpha$  and  $\beta$  sheets to  $d_{xz,yz}$ . The latter do not cross because of a small hybridization term. Also shown is the Fermi surface for a crystal field  $\Delta = 0.1$  eV. Since the  $d_{xy}$  van Hove singularity now lies below  $E_F$ , the  $\gamma$  sheet has turned from electron-like to hole-like.

Fig. 2 summarizes the variation of the  $t_{2g}$  orbital occupancies with onsite Coulomb energy  $U$ . In the case of Sr<sub>2</sub>RuO<sub>4</sub> ( $\Delta = 0$ ), a gradual charge transfer from  $d_{xz,yz}$  to  $d_{xy}$  states is found, in agreement with the trend found within QMC/DMFT for small  $U$  [7]. The system is seen to remain metallic up to very large  $U$ . This result is consistent with previous calculations [9] which revealed no Mott transition up to  $U = 4$  eV. Near  $U_c \approx 10$  eV the interorbital charge transfer is complete with  $n_{xy} = 1$ . The remaining half-filled  $d_{xz,yz}$  bands then undergo a Mott transition (see below).

Note that the filling of the  $d_{xy}$  band for  $\Delta = 0$  accelerates towards increasing  $U$ . The reason for this trend is that the larger  $d_{xy}$  occupancy reduces the intra- $t_{2g}$

screening of  $U$ . Since at the same time the occupancy of the  $d_{xz,yz}$  bands approaches one-half, the tendency for the latter bands to undergo a Mott transition becomes rapidly more favorable. In the absence of the  $d_{xy}$  band, the half-filled  $d_{xz,yz}$  bands (width  $W = 1.2$  eV) would exhibit a common metal insulator transition at  $U_c = 1.4$  eV, i.e., far below  $U = 10$  eV ( $U_c \approx 0.8W$  for twofold degenerate semicircular bands and  $J = U/4$  [16]). Thus the results for  $\Delta = 0$  may be interpreted as  $d_{xz,yz}$  Mott transition delayed by strong orbital fluctuations.

In view of this picture it is plausible that, at finite Ca concentrations, the greater initial occupancy of the  $d_{xy}$  band associated with  $\Delta > 0$  gives rise to complete  $d_{xy}$  filling and a  $d_{xz,yz}$  Mott transition at progressively lower values of  $U_c$ . This is confirmed by the results shown in Fig. 2. According to Fang *et al.* [14] the crystal field splitting for  $\text{Ca}_2\text{RuO}_4$  induced by octahedral distortions is about 0.4 eV. The  $d_{xy}$  band filling and  $d_{xz,yz}$  Mott transition is then shifted to  $U_c \approx 4$  eV. Thus, the reduced orbital fluctuations greatly diminish the delay of the Mott transition in the half-filled  $d_{xz,yz}$  bands. A slightly lower  $U_c$  would be obtained if other effects neglected so far, such as distortion induced band narrowing and interorbital hybridization [14], are taken into account.

In the range  $0.5 \leq x \leq 2.0$  the octahedral distortions consist mainly of rotations about the  $z$ -axis. The associated lowering of the  $d_{xy}$  band is rather small, giving  $\Delta \leq 0.2$  eV [14]. According to the results shown in Fig. 2, the correlation induced  $d_{xy}$  filling and  $d_{xz,yz}$  Mott transition then occur at  $U_c \approx 6$  eV. In this doping region the system therefore remains metallic. This result is consistent with angle resolved photoemission data [2] and optical data [3] which show that near  $x = 0.5$  all  $t_{2g}$  states are itinerant.

A crystal field  $\Delta = 0.1 \dots 0.2$  eV is large enough to push the  $d_{xy}$  van Hove singularity below  $E_F$ . This also agrees with the photoemission results [2] which yield nearly the same Fermi surface for  $\text{Ca}_{1.5}\text{Sr}_{0.5}\text{RuO}_4$  and  $\text{Sr}_2\text{RuO}_4$ , except that, because of the lowering of the van Hove singularity, the  $\gamma$  sheet has changed from electron-like to hole-like, as indicated in Fig. 1. These data are naturally explained by the results shown in Fig. 2, whereas they are difficult to reconcile with the trend towards half-filled  $d_{xy}$  bands proposed in Refs. [8, 12].

To prove that  $d_{xy}$  band filling and  $d_{xz,yz}$  Mott transition coincide we show in Fig. 3 the  $t_{2g}$  quasi-particle spectra for  $\Delta = 0.4$  eV. To avoid uncertainties stemming from the extrapolation from Matsubara frequencies to real frequencies we give here the spectra of the cluster Green's functions,  $A_i(\omega) = -\frac{1}{\pi} \text{Im} G_i(\omega + i\delta)$ , with  $\delta = 50$  meV. While spectral details differ from those of the solid [15], the cluster results are adequate for the distinction between metallic and insulating behavior. The spectra for  $U = 3.0$  eV reveal that all subbands are metallic and exhibit appreciable spectral weight below the single particle bands, associated with lower Hub-

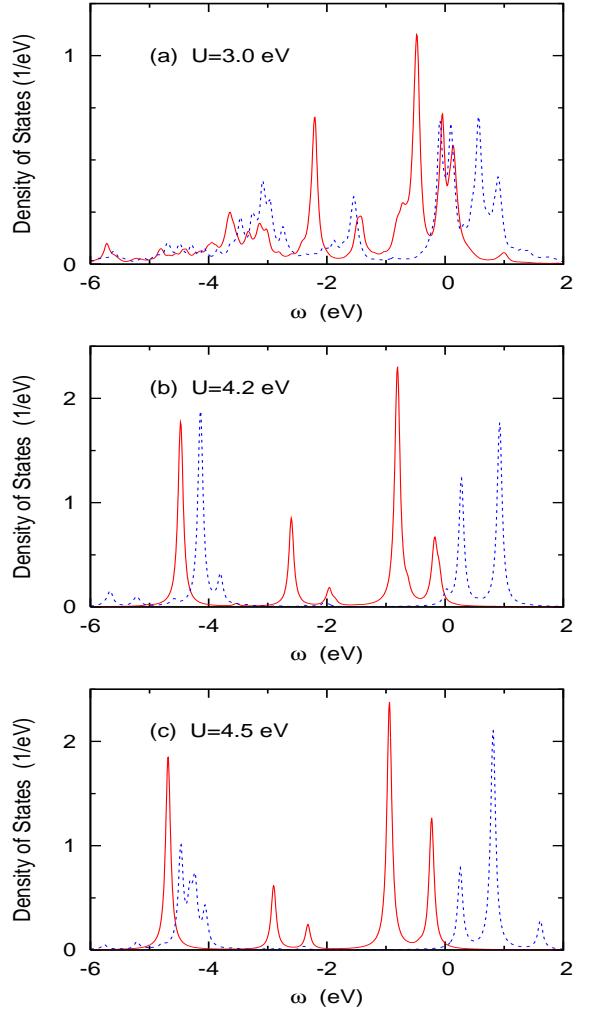


FIG. 3: Quasi-particle spectra calculated using ED/DMFT for crystal field splitting  $\Delta = 0.4$  eV;  $T = 20$  meV. (a) metallic region  $U = 3.0$  eV; (b) transition near  $U_c \approx 4.2$  eV; (c) insulating region  $U = 4.5$  eV. Solid (red) curves:  $d_{xy}$  band, dashed (blue) curves:  $d_{xz,yz}$  bands.

band bands. According to Fig. 2, the occupancies are  $n_{xy} = 0.84$  and  $n_{xz,yz} = 0.58$ . In contrast, at  $U = 4.5$  eV the  $d_{xy}$  band is filled and the half-filled  $d_{xz,yz}$  bands exhibit a clear separation into upper and lower Hubbard bands. The transition between these two regions occurs at  $U_c \approx 4.2$  eV. Note that the insulating gap arises between the filled  $d_{xy}$  band and the upper Hubbard bands of the half-filled  $d_{xz,yz}$  bands. The quasi-particle properties near this transition will be discussed elsewhere.

We point out that, in general, the  $d_{xy}$  band filling and  $d_{xz,yz}$  Mott transition do not need to take place at the same  $U$ . For instance, if the  $d_{xz,yz}$  bands were much wider, their Mott transition would occur above the  $d_{xy}$  band filling. Also, a stronger crystal field could give a  $d_{xy}$  filling at very small  $U$ , and a Mott transition in the half-filled  $d_{xz,yz}$  bands at a larger  $U$ . Because of the small

width of these bands the trend seen in Fig. 2 suggests that this possibility should arise only for  $\Delta > 0.5$  eV. An analogous effect was discussed by Manini *et al.* [17] for a two-band model with equal bands of semi-circular density of states, off-set via a crystal field  $\Delta$ . For unit total occupancy and small  $\Delta$ , a single transition was found where one band is pushed above  $E_F$  and the other (then half-filled) exhibits a Mott transition. For larger  $\Delta$ , one band is emptied at small  $U$  while the second remains metallic up to a Mott transition at larger  $U$ .

We also note that the Mott transitions in the  $3d^1$  perovskites  $\text{LaTiO}_3$  and  $\text{YTiO}_3$  studied by Pavarini *et al.* [18] reveal an almost complete emptying of two  $t_{2g}$  subbands, and a metal insulator transition in the remaining nearly half-filled band. Evidently, in all of these multi-band systems, the Mott transition is made feasible by a striking suppression of orbital fluctuations.

In the work discussed above the  $d_{xz,yz}$  bands are degenerate. In real  $\text{Sr}_2\text{RuO}_4$  these orbitals interact weakly, giving slightly different subband densities of states  $N_{xz\pm yz}(\omega)$  of identical width. Ca induced distortions will enhance these differences, so that the Mott transition in these subbands becomes non-trivial. This will be also addressed in future studies.

To analyze the Mott transition in  $\text{Ca}_{2-x}\text{Sr}_x\text{RuO}_4$  we have focused on the variation of the subband occupancies with Coulomb energy. In reality,  $U$  should be roughly constant as a function of  $x$ , with  $U \approx 3.1$  eV and  $J \approx 0.7$  eV according to constrained LDA calculations for  $x = 2$  [11]. Thus, in Fig. 2 a vertical line near  $U = 3$  eV should qualitatively cover the low temperature phase diagram.  $\Delta = 0$  with  $n_{xy} = 0.70$ ,  $n_{xz,yz} = 0.65$  corresponds to metallic  $\text{Sr}_2\text{RuO}_4$ .  $\Delta = 0.2$  eV with  $n_{xy} = 0.76$ ,  $n_{xz,yz} = 0.62$  represents the case  $\text{Ca}_{1.5}\text{Sr}_{0.5}\text{RuO}_4$ , which is also metallic. Finally, the results for  $\Delta \geq 0.4$  eV indicate that the metal becomes unstable since  $n_{xy}$  rapidly approaches unity and  $n_{xz,yz}$  one-half: the favorable electronic configuration for a Mott transition.

In summary, the paramagnetic metal insulator transition in the layer perovskite  $\text{Ca}_{2-x}\text{Sr}_x\text{RuO}_4$  has been investigated within multi-band finite temperature ED/DMFT. The results suggest a new concept following from the enhanced  $d_{xy}$  occupancy induced by Ca doping. Instead of orbital-selective Mott transitions, we find a common transition where the  $d_{xy}$  is completely filled and the remaining half-filled  $d_{xz,yz}$  bands undergo a standard metal insulator transition. In the pure Sr compound strong orbital fluctuations preclude this transition, despite the narrow width of the  $t_{2g}$  subbands. Thus, realistic Coulomb energies give rise only to a weak  $d_{xz,yz} \rightarrow d_{xy}$  charge transfer. This transfer is enhanced by the structural changes due to Sr $\rightarrow$ Ca substitution. Accordingly, orbital fluctuations are reduced and the ma-

terial becomes highly sensitive to local correlations. In the Ca rich compound orbital fluctuations are sufficiently weak that the Mott transition occurs at realistic values of  $U$ . On the basis of this picture it would be very interesting to study the region  $x \leq 0.5$  more closely in order to understand the orbital selective mass enhancement [3] and the rich magnetic phases of this material [1].

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- [1] S. Nakatsuji and Y. Maeno, Phys. Rev. Lett. **84**, 2666 (2000). S. Nakatsuji *et al.*, *ibid.* **90**, 137202 (2003); *ibid.* **93**, 146401 (2004); M. Braden *et al.*, Phys. Rev. B **58**, 847 (1998); O. Friedt *et al.*, *ibid.* **63**, 174432 (2001).
  - [2] S.-C. Wang, H.-B. Yang, A.K.P. Sekharan, S. Souma, H. Matsui, T. Sato, T. Takahashi, C. Lu, J. Zhang, R. Jin, D. Mandrus, E.W. Plummer, Z. Wang, and H. Ding, Phys. Rev. Lett. **93**, 177007 (2004).
  - [3] J.S. Lee, S.J. Moon, T.W. Noh, S. Nakatsuji, and Y. Maeno, Phys. Rev. Lett. **96**, 057401 (2006).
  - [4] Y. Maeno, T.M. Rice, and M. Sigrist, Phys. Today **54**, 42 (January 2001). A.P. Mackenzie and Y. Maeno, Rev. Mod. Phys. **75**, 657 (2003).
  - [5] T. Oguchi, Phys. Rev. B **51**, 1385 (1995); I.I. Mazin and D.J. Singh, Phys. Rev. Lett. **79**, 733 (1997).
  - [6] For a review, see: A. Georges, G. Kotliar, W. Krauth and M.J. Rozenberg, Rev. Mod. Phys. **68**, 13 (1996).
  - [7] A. Liebsch and A. Lichtenstein, Phys. Rev. Lett. **84**, 1591 (2000).
  - [8] V.I. Anisimov, I.A. Nekrasov, D.E. Kondakov, T.M. Rice, and M. Sigrist, Euro. Phys. J. B **25**, 191 (2002).
  - [9] A. Liebsch, EuroPhys. Lett. **63**, 97 (2003).
  - [10] S. Sakai, R. Arita, K. Held, and H. Aoki, Phys. Rev. B **74**, 155102 (2006).
  - [11] Z.V. Pchelkina, I.A. Nekrasov, Th. Pruschke, A. Sekiyama, S. Suga, V.I. Anisimov, and D. Vollhardt, cond-mat/0601507.
  - [12] X. Dai, G. Kotliar, and Z. Fang, cond-mat/0611075.
  - [13] Th. Pruschke and N. Grewe, Z. Phys. B **74**, 439 (1989).
  - [14] Z. Fang, N. Nagaosa, and K. Terakura, Phys. Rev. B **69**, 045116 (2004); Z. Fang and K. Terakura, Phys. Rev. B **64**, 020509(R) (2001).
  - [15] C.A. Perroni, H. Ishida, and A. Liebsch, Phys. Rev. B **75**, xxx (2007) [cond-mat/0609702]; see also: A. Liebsch, Phys. Rev. Lett. **95**, 116402 (2005); A. Liebsch and T.A. Costi, Eur. Phys. J. B **51**, 523 (2006).
  - [16] A. Liebsch, Phys. Rev. B **70**, 165103 (2004).
  - [17] N. Manini, G. Santoro, A. Dal Costa and E. Tosatti, Phys. Rev. B **66**, 115107 (2002).
  - [18] E. Pavarini, S. Biermann, A. Poteryaev, A.I. Lichtenstein, A. Georges, and O.K. Andersen, Phys. Rev. Lett. **92**, 176403 (2005).